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Development and Application of a Simple,  
Solid Integrating Ultraviolet Dosimeter,

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# I. Studies on the Chemistry of the Solid Integrating Ultraviolet Dosimeter

## Introduction

In studies previously reported, it has been shown that a simple solid system consisting of a halogenated hydrocarbon, a chromogenic proton acceptor and a solid matrix could be used for the integral measurement of ultraviolet light. The system is relatively stable, easily handled and amenable to casting in a variety of shapes. It is thus useful for measurement of topographic distribution of ultraviolet over irregular surfaces, as previously described for models of the human head. Within limits imposed by the frequency response of the system and the unsatisfactory color measurement equipment used in our early studies, it is possible to make meaningful estimates of the relative exposure of different areas on the surface. In the studies previously described, these difficulties were circumvented by matching the color of the exposed dosimeter with that of simultaneously exposed flat plaques of the same material, using time as the variable (rather than ultraviolet dose per se), and limiting time of exposure so that no significant change in solar spectral characteristics would be anticipated. Exposed areas were thus compared in terms of relative exposure time equivalents, permitting direct calculation of relative light distribution.

For general use as an integrator of erythema-effective ultraviolet energy, it is obviously necessary to establish a meaningful and reproducible relationship between the dosimeter response and the total erythema-effective energy. This is of particular importance if measurements are to be extended to relatively long intervals; during which appreciable spectral fluctuation of the incident light is to be expected. It is also desirable to be able to express absolute, rather than relative,

units of energy if at all possible. Furthermore, establishment of the response - energy relationship calls for more sophisticated and reliable methods for measuring both parameters than were previously available. Finally, it is necessary in order to evaluate dosimeter measurements, to determine the additivity of mixtures of different wave lengths of effective radiation, both in the dosimeter system and in the human skin. Investigations designed to permit measurement of additivity in the chemical system have already been initiated.

## II. Instrumentation:

In order to measure the spectral sensitivity of the dosimeter, it is necessary to have a source of light of reasonable spectral purity, and to be able to measure source output. In our studies to date we have used a Bausch and Lomb high intensity mercury monochromator, powered by a 200 watt mercury-xenon arc. Initially, flux measurements were made immediately before and after each irradiation, using a calibrated Eppley thermopile. For irradiations of appreciable duration there is some hope that these two readings will reflect the average variation in light flux during the exposure. In shorter time intervals, however, the appreciable arc wobble in the mercury lamp can introduce a considerable error. For this reason a system has been designed and constructed for the continuous sampling and integration of flux, to provide a reliable measure of dose. This was achieved by interrupting the monochromator exit beam with a quartz plate set at an angle of  $45^\circ$  to the light path. Approximately 96% of the incident light is transmitted to the sample, while approximately 4% is reflected at right angles to an adjacent photodetector. The response of the photodetector, and the slight variation in quartz reflectance with wave length were calibrated by

measuring the transmitted light with a thermopile. It was thus possible to establish a relationship between flux on the sample surface and response of the photodetector. By appropriate circuitry, the photodetector response was integrated to provide a direct measure of dose, and can be programmed to operate a servo-controlled shutter when the desired dose is reached. The system developed has various other capabilities, such as a programmed stepwise wave length drive, and the capacity to deliver constant or graded doses of energy to one sample or to several samples in series.

The existing monochromator, though useful, has several limitations, not the least of which is the dissimilarity of the spiked mercury arc to the approximate black-body characteristics of the sun. A monochromator presently being designed for other purposes will become available for later studies in this project. It will have the great advantage of enhanced spectral purity and stray light rejection, together with a light source (high-intensity xenon arc) which more closely approximates the emission spectrum of the sun.

A major source of difficulty in the original studies was quantitation of the observed color change. Although we were able to show a reasonably linear response of color measurement to the log of input dose, using a Photovolt Reflectance Meter with green ICI tristimulus filter, the procedure was inordinately time consuming, requiring continuous re-standardization of the instrument which drifted in both absolute value and span. It became apparent, furthermore, that there was no convenient method for comparing readings obtained at different times or under different conditions, because of span fluctuations. Finally, the available procedure for obtaining meaningful color values (ICI values) using this instrument called for three independent readings of each plaque through

the filter, with the attendant adjustments of span and zero for each, followed by a relatively onerous series of calculations which would greatly exceed in sophistication the results thus obtained.

Studies to be described in this report were obtained with the use of a Hunterlab Model D25 Color Difference Meter. While the differences between this instrument and the Photovolt previously used are manifold, the principal advantages for our application are: a high degree of instrumental stability; a geometrically meaningful relationship between the illumination (45°) and observation (90°) angles, permitting a meaningful estimate of diffuse reflectance; simultaneous observation of the sample by three calibrated and color-corrected phototubes; and digital readout in any of three associated coordinate scales. For our application we choose to abandon the ICI coordinates, which are polar, and use instead the Hunter L, a, b rectilinear system, in which L represents the lightness (grey scale) axis, a describes a red-green axis and b a yellow-blue axis. A subjective color is thus completely described by three numbers (ignoring sheen, haze, specular reflectance etc.) which may be readily reproduced by the use of suitable calibrated standards. By measuring the change in color associated with a specific dose increment, and calculating the vector  $\Delta c = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2}$ , it is possible to establish a reproducible relationship between dose and color change for a particular system.

As an additional aid to the study of the response parameters of the dosimeter system, we have available a Bausch and Lomb Model 505 recording spectrophotometer with an integrating globe reflectance accessory. This has proved valuable in studies of qualitative changes associated with the system and has given us some insight into the nature of the color change.

It is of value at this point to give some consideration to the distinctions between photometry and radiometry. The terms refer, respectively, to the measurement of light and to the measurement of radiation. Radiation can be and is defined in purely energetic terms throughout the entire electromagnetic spectrum; this includes the visible region, which is treated exactly like any other region (heat, radiowaves, x-ray, etc.). Photometry, strictly defined, refers to the measurement of light, and it must be recalled that the term "light" implies a visual phenomenon. Thus within the wave length band from about 400 mu to about 800mu we can distinguish a strictly objective measurement of energy and a partially subjective (and extremely complex) measurement of light.

Energy measurement is represented, in our case, by reflectance spectrophotometry. Since it is independent of subjective consideration, and can measure absorbance phenomena directly, it would appear to offer the better approach to quantitation of chemical changes. As pointed out previously however, the reaction in the dosimeter occurs initially at the exposed surface, gradually travelling deeper into the plaque. Thus the simple physical relationships observed in a uniformly colored material of infinite thickness are greatly complicated in dosimeter plaques irradiated for different periods of time. Furthermore, the nature of the change of the reflectance spectrum with irradiation is a broad decrease in reflectance ranging from the blue-green through the yellow-orange regions, with no notable region of maximum change. Thus a measured change at a specific wave length, though it would be a realistic estimate of a specific chemical change, would be a rather low sensitivity measurement technique.



The Color Difference Meter measures photometrically, i.e. it provides an instrumental analogue of a color sensation. Thus it is quite sensitive to minor color changes, and in addition it is quite reproducible. Because it represents a subjective phenomenon, however, it must be recognized that no simple relationship exists between measurement units and the chemical composition of the dosimeter. The three orthogonal coordinate scales are calibrated to estimate equal sensation differences, which involve a complex of the ratios of spectral components and of the absorption characteristics of visual pigments. As Wright has pointed out, it is not possible to tell "whether the subjectively equal steps correspond to equal arithmetic intervals in the magnitude of the sensation, equal geometrical ratios, or some other relation.-----

if we have four specimens, A, B, C and D, which have been chosen such that the intervals A-B, B-C and C-D appear equal, we cannot take it as axiomatic that the interval A-C is subjectively twice as great as the interval C-D". (Wright, W.D., The Measurement of Color, 3rd ed., 1964). For this reason, two distinct limitations must be recognized in the interpretation of dose-color change relationships. First, they are applicable only over the color range measured. Secondly, any graphical relationship observed is likely to hold only for a limited range, and its dimensions are unlikely to have fundamental significance. In our early studies with the Photovolt (which does not estimate subjective changes directly), we reported a relationship between the green-filtered reflectance and the log of ultraviolet dose. With the Hunter meter we have found a reasonably linear relationship between  $\log \Delta c$  (color change vector) and dose<sup>-1</sup> (or its analogue, time<sup>-1</sup>). Both relationships can be useful, but neither is likely to describe the basic process.

### III. Nature of the dosimeter reaction:

Several lines of evidence described in our previous report indicated that the principal reaction involved free-radical mediated production of HCl, followed by interaction of the proton with the chromogenic indicator. Direct ionization could not be expected at the energy level of wave lengths studied, and would not be consistent with the very rapid increase in efficiency between 3600Å and 3200Å. The relative effectiveness of different halogenated compounds, furthermore, appeared consistent with their expected ability to produce halogen free-radicals. The acidic nature of the chromogenic reaction was indicated by the absolute requirement for a hydrogen-containing component, and by the competition of the relatively strong base Dibenzylamine. Further evidence pertaining to the reaction mechanism was provided by the following procedures. Plaques were prepared in multiple layers by allowing the first layer to cool completely, before adding the second layer just above solidification temperature. The adequacy of this procedure was tested by pouring alternate layers of wax and of methyl yellow-containing wax, and examining cross-sections of the results. In all cases clear interfaces with no gross evidence of diffusion were obtained. Plaques were then prepared in which the one layer consisted of 3 ml paraffin containing 0.1 µM methyl yellow per ml., and the second of 4 ml paraffin containing 0.2 µM hexachlorocyclopentadiene per ml. The plaques were exposed to a Westinghouse sun lamp for periods of one hour or more. At the end of this time a very narrow but clearly visible region of color change was visible at the interface, in cross-sections, in those plaques in which the side containing the halogen source was exposed to the light. When the side containing the dye was uppermost, no interfacial reaction was observed. This indicates that methyl yellow served to screen the

effective wave lengths of light and in this manner might well inhibit, rather than catalyzing, the fundamental reaction with light. That the screening effect was not merely due to the depth of the paraffin layer was proved by pouring a 4 ml layer of paraffin over a 3 ml layer containing  $0.1\ \mu\text{M}$  methyl yellow and  $0.2\ \mu\text{M}$  hexachlorocyclopentadiene per ml. Exposure of such plaques with the paraffin side uppermost produced a distinct color change which was not, however, limited to the interface.

To determine finally whether methyl yellow was directly involved in the principal interaction, plaques were prepared consisting of the following three layers: 2 ml containing  $1.0\ \mu\text{M}$  methyl yellow per ml; 2 ml containing either no additive or  $0.1\ \mu\text{M}$  dibenzylamine per ml; 2 ml containing  $5\ \mu\text{M}$  hexachlorocyclopentadiene per ml. Irradiation as described previously, with the dye uppermost, produced no visible change in any plaque. When the halogen source was exposed, a clear zone of color change was observed at the dye-dibenzylamine interface; no change could be seen at the dibenzylamine-halogen source interface. In those plaques in which dibenzylamine was omitted from the middle layer, no color change was observed. These studies appear to demonstrate conclusively that the initial reaction is that of the halogen source with the effective radiation; that methyl yellow is not required for the reaction and may in fact compete for the reaction-producing photons; and that a reaction product which will not diffuse through paraffin, but can be transported through a paraffin layer which contains dibenzylamine, will produce a color change in methyl yellow. These data appear to point directly to the production of protons following interaction of light with the halogen source (systems containing no halogen source are completely inert). Though no direct evidence of free radical mechanism is offered,

the previously mentioned objections, plus the effective filtering action of methyl yellow argue against direct ionization as a mechanism. A further objection is the fact that the halogen source used contains no hydrogen in its molecule.

#### IV. Effect of composition on sensitivity and stability

For studies of total sensitivity of the system, irrespective of wave length, plaques were irradiated under the Westinghouse sun lamp using time as the criterion of dose (after a brief warm-up the lamp output is quite stable over periods of several hours). Initial studies with both monochromatic and polychromatic light indicated that a large component of the color change gave a straight-line relationship between  $\log \Delta c$  (color change vector) and reciprocal dose or time. For comparative values the best straight line was calculated by the method of least squares and the Y-intercept was interpolated (i.e. color change at infinite dose). Changes in the value of the Y-intercept represent changes in the capacity of the system. From this value and the slope of the regression line, the half-time ( $T_{1/2}$ ) or the half-dose ( $D_{1/2}$ ) were calculated. As a measure of the sensitivity of the system (time or dose producing a half-maximum color change). Since we have previously pointed out the limitations of arithmetic interpretations of the color scale, our conditions of comparison should be emphasized:

1. Extrapolation to the Y-axis was always very short, since irradiations were always continued until no further discernible color changes were occurring.

2. The  $T_{1/2}$  values were always well within the region of linearity of the relationship.

3. Comparisons were limited to systems with essentially similar Y-intercepts, so that the  $T_{1/2}$  values represented approximately identical colors and thus, presumably, identical chemical compositions. Comparison between systems with dissimilar end-points or in which the end-point requires extensive extrapolation are unlikely to be valid.

A number of studies have been designed to evaluate the variables of the dosimeter system. It had been noted that the response of different batches of the same nominal composition often showed variable responses. The heating time involved in melting the wax system, dissolving the reactants and driving off the volatile diluting solvents (hexane and methanol) were investigated. Two batches of similar composition, one of which had been prepared and partially used previously, were melted and a batch of plaques were poured. The mixtures were allowed to cool, then were remelted and further plaques were prepared. As shown in Table I, the sensitivity of the fresh batch was reduced by reheating to a level corresponding to that of the older batch. There was little further effect from reheating the older system. The total capacities of the systems were little affected by the treatments. It appears likely that the fresh mixture contained a low level of acid contamination, either as spontaneously generated HCl in the halogen component or a free acid in the dye. The studies indicated the desirability of a short equilibration period in freshly prepared mixtures.

It was reported previously that dibenzylamine (DBA) inhibited color production in proportion to its concentration. In order to determine whether this effect occurred at the expense of the total capacity of the system, plaques were prepared in which DBA concentration was varied in relation to two levels of hexachlorocyclopentadiene (HCCPD) and a fixed level of methyl yellow (MY). Irradiation of these systems produced

the results shown in Table II. Addition of even low levels of DBA slowed the reaction somewhat, while the presence of a 5 to 1 excess of DBA over the other two components completely prevented color changes. At a moderately high level of HCCPD, an approximately normal, though rather slow total change occurred even when DBA exceeded MY by 5 to 1. Most surprising, however, was the fact that DBA increased, rather than decreased the capacity of the system at levels up to one-half that of methyl yellow, under conditions in which the halogen source was presumably limiting. It is conceivable that the DBA, acting as a more efficient proton scavenger than the MY, actually increases the effective yield of acid by preventing its escape at the surface of the system. The fact that the total system capacity is lowered by the addition of HCCPD, and brought back to normal by the addition of even a trace of DBA, supports the surface-loss concept. The presence of a relatively high concentration of HCCPD near the surface could result in HCl production greatly in excess of the capacity of immediately adjacent MY to trap it. Thus surface loss would be accelerated while deeper layers of the system would be screened by the high surface absorption of ultraviolet. The presence of DBA, previously shown to be an excellent proton distributor in paraffin, would result in more effective retention of the surface-generated HCl. Regardless of its mechanism, DBA is a highly effective additive for slowing the reaction system without inhibiting its response capacity.

The total response range of a system in terms of color production should be a function of methyl yellow concentration, provided that the halogen source is present in excess. This was studied by varying the MY at constant, relatively high HCCPD level. DBA was also varied

at each MY concentration. The results, shown in Table III, indicate that the system capacity is related to MY level, at least within the range studied. At the zero levels of DBA, it can be seen that the capacity value increased from 13.0 to 20.2 to 29.9 units at the three levels of MY used. It seems improbable that a higher level of MY would produce a response, since it is already present in excess of the halogen level. Surprisingly, levels of DBA which were as high as or higher than those of MY enhanced the color range, even when halogen should have been limiting. In fact the enhancement of the total range by DBA at the highest level of MY is quite impressive, and further emphasizes the ability of this compound to stabilize the reaction products.

While color produced in the dosimeter reaction generally appeared to be stable, it was noted that plaques which were left on the stage of the color difference meter appeared to change somewhat in value. The studies outlined in Table IV were designed to investigate this phenomenon.

In trials 1 and 2, which were similar, it was established that a distinct color reversion occurred during a 5 minute post-irradiation period. The effect was more or less independent of the total change induced by irradiation, and appeared to be largely confined to the L scale, although some change in the a scale was also noted. No appreciable change occurred in unirradiated plaques under the same conditions.

The third trial, in which relatively larger reversionary changes were noted for unknown reasons, demonstrated that removal of plaques from the illuminated stage of the instrument between readings was an effective method for preventing reversion. Thus some type of "re-

activation" process appeared to result either from intense illumination or from the somewhat elevated internal temperature of the viewing head. The effectiveness of removing the plaques was confirmed by trial 4, in which only minor changes were noted. (Reading a plaque requires approximately 10-15 seconds).

In trial 5 it was demonstrated that color reversion was a continuing process, at least for 10 minutes. When the plaque was retained in place but the illumination level reduced between readings, some reduction of effect was observed, indicating that the internal heat of the viewing head was at least not the entire cause of the changes. Similarly, trials 6 and 7, in which some plaques were partially shielded from internal heat by a covered slip (and, at the same time, were prevented from losing HCl at the surface), showed a rather small protective effect which could have been the result of transmission and reflection losses in the visible light component (illuminated at  $45^\circ$ ).

Since stability of the color produced is essential for utilization of the system, and in view of the possibility of fading introduced in the previous study, an experiment was designed to test the long term stability of an irradiated system. Since irradiated plaques often have only a relatively thin surface "film" of color change, and since equilibration between adjacent protonated and non-protonated MY molecules might diffuse the color and thus reduce its intensity, a large plaque was half covered with opaque material, and the uncovered portion was irradiated long enough to produce a marked color change which extended several millimeters below the surface. A series of readings was obtained from each side of the dividing line at intervals of from one minute to three weeks. Between readings the plaque was stored under



under normal conditions of laboratory illumination, with no special effort to protect it from visible light. The results in Table V show only minor random change in the L component of the irradiated side. It will be recalled that L scale fading was the principal change in plaques left on the color difference meter stage. A small though distinct loss of a scale reading was observed, primarily during the first 24 hours of a scale. The b scale readings showed small random changes.

The small long term changes in the L and b scale readings of the unexposed side were in the direction of the normal response to ultraviolet light, and might represent the effect of laboratory illumination. No long term changes in the a scale were observed however. It appears therefore, that the color change in this dosimeter system is highly stable provided that continued very high levels of illumination are avoided.

#### V. Effectiveness of different halogen sources:

In the previous report other halogen sources were mentioned as being effective in this system, though generally less so than HCCPD. The relationship between the activity of halogenated compounds and their spectral sensitivity is of great interest to us. Two preliminary trials will be mentioned briefly. In the first of these, a gross comparison was made between the relative sensitivity of different halogens under two light sources, the Westinghouse sun lamp (primarily 2800-3300 Å) and the black light (primarily 3660 Å). No attempt was made to quantitate the emission of the sources, but Y-intercepts and half-times were calculated (with a much lower confidence level than in previously cited studies, due to the very long times involved). The

halogenated compounds were used at levels to provide a total halogen content equal to that provided by 0.01  $\mu\text{M}$  per ml HCCPD. In other words, bistrichloromethylbenzene, hexachloroethane, hexachlorobutadiene and hexachlorobenzene were used at 0.01  $\mu\text{M}$  per ml., perchlorofulvalene at 0.005  $\mu\text{M}$  per ml., tetrachlorotoluene at 0.015  $\mu\text{M}$  per ml., and trichlorotoluene and trichlorobenzene at 0.02  $\mu\text{M}$  per ml. The results, presented in Table VI, show that perchlorofulvalene is appreciably more sensitive than is HCCPD, and that its relative sensitivity to 3660 Å is also much greater. Of the others tested, bistrichloromethylbenzene, tetrachlorotoluene and hexachloroethane showed decreasing orders of crudely measurable sensitivity to the sun lamp, while slight activity was detectable in the case of trichlorotoluene and of hexachlorobutadiene under the sun lamp. Only HCCPD and perchlorofulvalene were sensitive to the black light, and no activity was shown by the benzene derivatives lacking side-chain halogens (mono-, tri-, and hexachlorobenzene). Table VII shows the effect of addition of DBA to the moderately active systems. The effect with perchlorofulvalene was similar to that described earlier for HCCPD, namely, an increase in the capacity of the system. Increases in both capacity and sensitivity were noted with the side chain-halogenated toluene derivatives, bistrichloromethylbenzene and a,a,2,6-tetrachlorotoluene. Hexachloroethane, rather surprisingly, showed a marked increase in sensitivity with no apparent change in capacity. The reliability of the Y-intercept for this compound in the absence of DBA is, however, very low.

The above data lends support to the idea that less active compounds may show a higher degree of discrimination against low-energy quanta. Since one objection to HCCPD is its slight but real sensitivity

to wavelengths appreciably longer than the human erythema spectrum, such compounds would be of great interest in formulating a field dosimeter. We have begun to study some of the action spectra of these compounds, but since such studies are necessarily cumbersome and extremely time consuming, only fragmentary data are presently available. Table VIII shows some of these values, presented as relative sensitivity at different wave lengths independent of the absolute sensitivity of the compound. Thus the highly active perchlorofulvalene and the very slightly active hexachloroethane are both shown as having 100% relative activity at 3100 A, though the absolute activities differ by orders of magnitude. It is extremely difficult to obtain activity data on such compounds in a form permitting direct comparisons between compounds, so for the present we are measuring only initial reaction rates and using these as crude indices of wave length-specific activity within a single compound. Each value is computed from the color change occurring in duplicate sets of seven plaques exposed to graded doses of monochromatic radiation with the instrumentation described earlier in this report.

In confirmation of hypothesis, the highly active perchlorofulvalene is relatively sensitive to 3600 A and has its activity maximum in the 3200 A region (HCCPD maximum is approximately 3150 A). The three moderately active compounds, hexachloroethane, bistrichloromethylbenzene and tetrachlorotoluene show no activity at 3600 A and indicate activity peaks at or above 3200 A, between 3100 and 3200 A, and below 3100 A respectively. The relatively inert hexachlorobutadiene has its maximum in the 2900-3100 A range and shows an appreciable decrease in activity at 3200 A, while the almost inert trichlorobenzene

showed no detectable activity at 3100 Å and indicated an activity peak below 3000 Å. The apparently high sensitivity maximum of the low activity trichlorotoluene is considered anomalous at this point.

We are greatly encouraged by this indication that spectral selectivity may be varied and to some extent predicted on the basis of the sensitivity of the halogen source. In addition to extending and refining these spectral sensitivity investigations, we hope to evaluate the effect on spectral sensitivity of dibenzylamine, with its interesting sensitizing-desensitizing capabilities. We will also extend our studies to include other halogenated compounds, with special attention to ring-substituted compounds including those with slightly less aromatic rings than benzene (e.g. naphthalene). It is our hope to develop a system having a sensitivity spectrum essentially identical to that of the skin at the longer wave lengths, and to establish clear numerical parameter relating its color response to incident dose of ultraviolet light.

VI. Studies of distribution of ultraviolet radiation over the human head:

The studies of the effect of global, sky and reflected radiation reported in the first annual report, have been extended and repeated, using the Hunter Color difference meter to obtain more accurate information about the amount of radiation reaching various areas of the human head. In these experiments, essentially similar arrangements of eclipse and reflection shades (as previously reported) were utilized. 1 inch square pieces of the wax dosimeter were gently peeled off the dipped mannequin heads after constant exposures to the sun, flattened by very gentle heating, and then read for L, a, b scales on the Hunter meter. The results of these experiments, expressed as % dose of

that reaching the vertex are shown in Table IX. It appears that at a sun angle of  $65^\circ$ , the orbital area, upper lip, nasolabial fold and anterior neck received approximately less than 20% of the radiation reaching the scalp. An eclipse shade reduces the amount reaching the scalp and nose by about 35%, or about that expected to come directly from the sun. (for latest data of Solar UV radiation, see Bener, AFCRL-63-654 report, 1963). There is practically no effect on normally shaded areas. On ordinary reflecting surfaces (Albedo 5%), a reflection shade has no significant effect.

Repetition of the experiments using a highly reflective surface wiped out all the differences in radiation due to anatomic shielding, the eclipse shade had only about a 15% reducing effect, but addition of a reflection shade caused a very significant reduction of radiation reaching normally shaded areas.

#### Instrumentation:

Automation of the Bausch and Lomb monochromator, as outlined in the last renewal application has been accomplished. In principle, the monochromator has been fitted with a solenoid operated shutter, in front of which is placed a 1 mm thick optically flat, quartz plate, located at  $45^\circ$  to the exit beam. This plate reflects 4% of the radiation to a phototube, sensitive primarily in the ultraviolet region. The current from the phototube is suitably amplified and stored in condensers. An electronic net work registers the amount of current obtained, and actuates the shutter, so that it closes after a given dose of radiation is delivered. The control instrument is designed to allow for correction for differences in sensitivity of the phototube at different wavelengths. A small motor is fitted to the wave length guide of the

monochromator, so that by appropriate pre-setting a sequence of doses of the same, or at different (predetermined) wave lengths may be delivered. The target may be the dosimeter, in which case provisions have been made to advance plaques into the beam after each exposure, or the human skin. The instrument is extremely versatile, and can be easily operated by technical help.

A high intensity, narrow band pass, virtually stray-light free double monochromator for human studies is under construction.

TABLE I

EFFECT OF OVERHEATING DOSIMETER MIXTURE

PLAQUES CONSISTED OF 7 ML. WAX CONTAINING 0.1  $\mu$ M METHYL YELLOW (MY) AND 0.1  $\mu$ M HEXACHLOROCYCLOPENTADIENE (HCCPD) PER ML. BATCH 1 WAS THE RESIDUE OF A MIXTURE WHICH HAD BEEN HELD MOLTEN FOR SEVERAL HOURS THE PREVIOUS DAY. BATCH 2 WAS PREPARED FRESH. VALUES DERIVED FROM EIGHT TO ELEVEN TIMED READINGS ON EACH OF TWO PLAQUES PER TREATMENT.

<u>BATCH</u>	<u>TREATMENT</u>	<u>T<sub>1/2</sub> (MINUTES)</u>	<u>ANTILOG Y-INTERCEPT ( . C UNITS)</u>
1		3.9	21.0
2		2.2	19.8
1	REHEATED	3.5	19.6
2	REHEATED	3.8	19.0

TABLE II

EFFECT OF DIBENZYLAMINE (DBA) CONCENTRATION

PLAQUES CONTAINED 7 ML WAX WITH THE SPECIFIED COMPOSITION. OTHER CONDITIONS AS IN TABLE I.

COMPOSITION ( $\mu$ M PER ML)			$T_{1/2}$ MINUTES	ANTILOG Y-INTERCEPT ( $\mu$ C UNITS)
<u>MY</u>	<u>HCLPD</u>	<u>DBA</u>		
0.1	0.1	0	3.7	32.4
0.1	0.1	0.01	4.4	34.1
0.1	0.1	0.05	15.9	39.0
0.1	0.1	0.10	32.2	35.6
0.1	0.1	0.50	NO CHANGE	
0.1	0.4	0	1.0	23.7
0.1	0.4	0.01	1.2	31.1
0.1	0.4	0.05	1.8	28.6
0.1	0.4	0.10	5.2	33.2
0.1	0.4	0.50	14.1	28.2



TABLE III

EFFECT OF METHYL YELLOW CONCENTRATION

CONDITIONS AS IN TABLE II

<u>MY</u>	<u>CONCENTRATION (<math>\mu</math>M PER ML)</u>		<u>T<sub>1/2</sub> (MINUTES)</u>	<u>ANTILOG Y-INTERCEPT (<math>\pm</math> C UNITS)</u>
	<u>HCCPD</u>	<u>DBA</u>		
0.025	0.4	0	0.7	13.0
0.025	0.4	0.01	0.8	15.8
0.025	0.4	0.05	2.4	16.5
0.05	0.4	0	0.7	20.2
0.05	0.4	0.01	0.8	23.1
0.05	0.4	0.05	2.9	26.5
0.5	0.4	0	1.2	29.9
0.5	0.4	0.05	4.3	49.4
0.5	0.4	0.50	29.1	46.0

TABLE IV

REVERSION OF COLOR CHANGE UNDER INTENSE ILLUMINATION

IRRADIATION TIME AS INDICATED. READINGS AT 0 AND 5 MINUTES AFTER IRRADIATION. ILLUMINATION CONTINUOUS UNLESS OTHERWISE INDICATED. DATA SHOW REDUCTION OF IRRADIATION - INDUCED CHANGE OVER 5 MINUTES (REVERSION TOWARD PREIRRADIATION COLOR). PARENTHETIC VALUES SHOW CHANGES AWAY FROM PREIRRADIATION COLOR, OR CHANGES IN UNIRRADIATED PLAQUES. COMPOSITION : 0.1  $\mu$ M MY AND 0.1  $\mu$ M HCCPD PER ML.

	<u>IRRADIATION (MINUTES)</u>	<u>A L</u>	<u>A</u>	<u>B</u>
TRIAL 1	0	(+0.2)	(-0.1)	0
	2	3.5	2.8	1.0
	4	1.8	(-0.2)	(-0.4)
	6	2.8	0.9	1.0
	8	2.2	0.4	0
	10	2.0	0.5	(-0.2)
TRIAL 2	1	2.7	1.8	0.4
	2	1.3	(-0.1)	(-0.6)
	4	2.0	0.2	(-0.3)
	6	1.9	0	(-0.4)
	8	2.4	0.6	(-0.2)
	10	1.7	0.3	0
TRIAL 3	4	5.3	4.3	2.2
	8	4.6	1.8	1.1
	4*	0.7	1.4	(-0.1)
	8*	0.4	0.6	0
TRIAL 4	0*	( 0.1)	(-0.2)	( 0.1)
	1*	0.5	0	(-0.2)
	1*	0.2	0.2	(-0.3)
	2*	1.0	0	(-0.7)
	4*	0	(-0.6)	(-0.2)
	6*	0.7	0	(-0.5)
	8*	0.2	0	(-0.3)
TRIAL 5	1	0.9	0.7	0
	1**	1.6	1.5	0.2
	1***	1.1	0.9	0
TRIAL 6	1	0.7	0.2	0
	2	0.7	0.4	(-0.1)
	4	0.8	(-0.1)	(-0.2)
	1 <sup>oo</sup>	0.8	0.1	0.1
	2 <sup>oo</sup>	0.5	0.1	0.1
	4 <sup>oo</sup>	0.5	0.1	0.1
TRIAL 7	1	0.7	0.8	0
	2	1.1	1.4	0.1
	4	1.3	1.5	0.1
	6	2.6	2.6	1.0
	1 <sup>oo</sup>	0.4	0.4	0
	2 <sup>oo</sup>	0.6	0.7	0.2
	4 <sup>oo</sup>	1.4	1.5	0.5
	6 <sup>oo</sup>	1.7	1.7	0.7

FOOTNOTE- \* PLAQUE REMOVED FROM ILLUMINATION BETWEEN READINGS

\*\* CHANGE IN TEN MINUTES

o ILLUMINATION LEVEL REDUCED BETWEEN READINGS

oo PLAQUES VIEWED THROUGH COVER SLIP

TABLE V

COLOR DIFFUSION WITHIN A PLAQUE

A LARGE PLAQUE CONTAINING 0.5  $\mu$ M MY AND 0.5  $\mu$ M HCCPD PER GRAM (DENSITY 0.72) WAS HALF COVERED WITH AN OPAQUE MASK AND IRRADIATED WITH THE SUN LAMP FOR 5 MINUTES. READINGS WERE TAKEN ON EACH HALF, ADJACENT TO THE DIVIDING LINE, FOR THREE WEEKS.

<u>TIME</u>	<u>UNIRRADIATED</u>			<u>IRRADIATED</u>		
	<u>L</u>	<u>A</u>	<u>B</u>	<u>L</u>	<u>A</u>	<u>B</u>
1 MINUTE	36.4	-1.6	19.1	26.4	8.6	11.5
2 "	35.9	-1.6	19.2	25.8	8.6	11.8
4 "	36.1	-1.6	19.2	26.8	8.2	11.4
12 "	36.6	-1.9	19.3	27.4	8.2	11.1
20 "	36.3	-2.0	19.3	27.1	7.8	11.3
60 "	35.7	-1.8	19.0	27.3	7.3	11.1
120 "	35.8	-1.8	19.1	27.5	6.5	10.7
1 DAY	35.0	-1.5	18.2	27.6	5.4	11.1
2 "	34.2	-1.3	18.3	27.4	5.2	11.4
7 "	33.9	-0.8	18.6	26.3	5.6	11.7
14 "	33.7	-1.0	18.6	26.4	5.3	12.0
21 "	34.0	-1.5	18.6	26.8	5.0	12.3

TABLE VI

SENSITIVITY OF DIFFERENT HALOGEN SOURCES

PLAQUES CONTAINED 0.10  $\mu\text{M}$  OF MY AND .01  $\mu\text{M}$  (OR EQUIVALENT-SEE TEXT) OF HALOGEN SOURCE PER ML, AND WERE IRRADIATED UNDER THE SUN LAMP (S) OR BLACK LIGHT (3660  $\text{\AA}$ ) (B). OTHER CONDITIONS AS DESCRIBED PREVIOUSLY.

HALOGEN SOURCE	LIGHT SOURCE	$T_{1/2}$ (MINUTES)	ANTILOG Y-INTERCEPT ( $\Delta C$ UNITS)
HEXACHLOROCYCLOPENTADIENE		3.7	16.9
		17.8	9.9
PERCHLOROFULVALENE	S	0.9	22.6
	B	1.5	25.5
1,4-BIS-TRICHLOROMETHYL BENZENE	S	15.7	18.1
	B	ND	
A,A,2,6-TETRACHLOROTOLUENE	S	39.1	6.0
	B	ND	
A,2,4- TRICHLOROTOLUENE	S	D	
	B	ND	
MONOCHLOROBENZENE	S	ND	
	B	ND	
1,2,4-TRICHLOROBENZENE	S	ND	
	B	ND	
HEXACHLOROETHANE	S	54.9	23.8
	B	ND	
HEXACHLOROBUTADIENE	S	D	
	B	ND	
HEXACHLOROBENZENE	S	ND	
	B	ND	

D = DETECTABLE CHANGE AT 30 MINUTES. ND = NO DETECTABLE CHANGE.

TABLE VII

EFFECT OF DBA ON SENSITIVITY OF HALOGEN SOURCES

PLAQUES AS IN TABLE VI WITH ADDITION OF 0.025 $\mu$ M DBA PER ML, IRRADIATED UNDER SUN LAMP. CONTROL DATA REPEATED FROM TABLE VI.

<u>HALOGEN SOURCE</u>	<u>DBA</u>	<u>T<sub>1/2</sub> (MINUTES)</u>	<u>ANTILOG Y-INTERCEPT (<math>\Delta</math>C UNITS)</u>
PERCHLOROFULVALENE	-	0.9	22.6
	+	0.8	33.3
1,4-BISTRICHLOROMETHYL BENZENE	-	15.7	18.1
	+	4.8	33.9
A,A,2,6-TETRACHLOROTOLUENE	-	39.1	6.0
	+	4.8	30.3
HEXACHLOROETHANE	-	54.9	23.8
	+	4.1	23.0

TABLE VIII

SPECTRAL SENSITIVITY OF VARIOUS HALOGEN SOURCES  
RELATIVE TO SENSITIVITY AT 3100 Å°

<u>HALOGEN SOURCE</u>	<u>WAVE LENGTH (Å°)</u>					
	<u>2800</u>	<u>2900</u>	<u>3000</u>	<u>3100</u>	<u>3200</u>	<u>3600</u>
A, A, 2, 6-TETRACHLOROTOLUENE	32			100	53	ND
A, 2, 4-TRICHLOROTOLUENE	53			100	119	ND
1, 2, 4-TRICHLOROBENZENE	100		44	ND*		ND
PERCHLOROTULVALENE	20			100	135	18
1, 4-BISTRICHLOROMETHYL BENZENE	63			100	100	ND
HEXACHLOROETHANE	57			100	128	ND
HEXACHLOROBUTADIENE	87	118		100	74	ND

\* ACTIVITY NOT DETECTED AT 3100 Å°. EXPRESSED RELATIVE TO 2800 Å°.

# DISTRIBUTION OF ULTRAVIOLET RADIATION OF THE HUMAN HEAD

## GLOBAL RADIATION

Schematic diagram of path taken by UV radiation from sun, sky and ground. The area below the dome of the "sky" represents greater intensity of UV radiation near the sun. Note large amount and multidirectionality of sky radiation.



### % Color Change

Scalp	100%
Orbit	18%
Zygoma	48%
Nose	83%
Upper Lip	18%
Ant. Neck	14%

Mannequin coated with Doulider exposed on cloudless day. Note relative exposure of orbit, upper lip, lateral cheeks and anterior neck. H 80° Albedo 5%.



### % Color Change

Scalp	99%
Orbit	32%
Zygoma	89%
Nose	93%
Upper Lip	95%
Ant. Neck	97%

Presence of a highly reflecting surface (white sand) markedly affects previously protected areas. H 65° Albedo 35%.

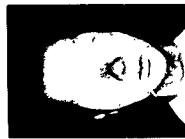


A 'Reflexion Shade' used with a 'Reflexion Shade' usually excludes all but stray UV radiation. H 65° Albedo 35%.

## SKY AND REFLECTED RADIATION



'Eclipse Shade' stops sun radiation only. Note considerable amount of sky and reflected radiation still reaching the head. Experimental situation simulates beach umbrella or parasol.



### % Color Change

Scalp	87%
Orbit	18%
Zygoma	47%
Nose	83%
Upper Lip	18%
Ant. Neck	10%

'Eclipse Shade' reduces incident UV by about 85%, even though Mannequin head is now in the shade. H 80° Albedo 5%.



### % Color Change

Scalp	86%
Orbit	48%
Zygoma	81%
Nose	90%
Upper Lip	93%
Ant. Neck	93%

In presence of a highly reflecting surface, 'Eclipse Shade' has very little effect. Thus an umbrella is of little use on a sandy beach. H 80° Albedo 35%.



'Everyone knows' that water reflects UV radiation as we proceed. Result: No evidence of significant UV reflection.

## SKY RADIATION ALONE



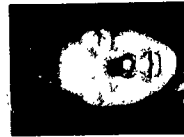
'Eclipse Shade' stops sun radiation. 'Reflexion Shade' stops ground reflection. A significant amount of 'sky' radiation still reaches the model.



### % Color Change

Scalp	87%
Orbit	14%
Zygoma	38%
Nose	41%
Upper Lip	10%
Ant. Neck	8%

Addition of a 'Reflexion' shade has little effect on color change as expected, since Albedo is only 5%.



### % Color Change

Scalp	72%
Orbit	38%
Zygoma	43%
Nose	47%
Upper Lip	32%
Ant. Neck	19%

Addition of a 'Reflexion Shade' reduces incident radiation with only a slight effect on color change. H 80° Albedo 35%.



Most people have hair, particularly women. This mannequin head was exposed with a female wig in place. H 80° Albedo 35%.